

A decline in tropospheric organic bromine

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[1] Recent changes in atmospheric bromine (Br) are estimated from samples collected at ten globally distributed, ground-based sites. The results indicate that the global tropospheric burden of Br from the sum of halons and methyl bromide (CH₃Br) peaked in 1998 and has since declined by nearly 5% (or 0.8 ± 0.2 pmol mol⁻¹ or ppt). These changes are driven primarily by a decrease of CH₃Br since 1998 that is about two times larger than expected given reported declines in industrial production, a result that may suggest revisions to our understanding of the global atmospheric budget for this gas. The observations imply 25–30% larger declines in the atmospheric burden of ozone-depleting, total equivalent chlorine (ECI = Cl + Br*45) in recent years than noted previously. **INDEX TERMS:** 0300 Atmospheric Composition and Structure; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Montzka, S. A., J. H. Butler, B. D. Hall, D. J. Mondeel, and J. W. Elkins, A decline in tropospheric organic bromine, *Geophys. Res. Lett.*, 30(15), 1826, doi:10.1029/2003GL017745, 2003.

1. Introduction

[2] Bromine from halons and methyl bromide more than doubled in the atmosphere from the mid-1900s to 1995 [Butler *et al.*, 1999; Fraser *et al.*, 1999; *World Meteorological Organization (WMO)*, 2003]. This increase, along with a concurrent increase in atmospheric chlorine (Cl), has led to the depletion of stratospheric ozone [WMO, 2003]. While Cl from long-lived gases has decreased since 1993–1994 in the lower atmosphere [Montzka *et al.*, 1996; Cunnold *et al.*, 1997], much concern remains over increases in atmospheric Br because it is nearly 50 times more efficient than Cl for destroying stratospheric ozone [Daniel *et al.*, 1999; WMO, 2003].

[3] Bromine from halons continues to increase in the atmosphere because of ongoing use of remaining stocks, and because of continued production allowed under the Montreal Protocol on Substances that Deplete the Ozone Layer [United Nations Environment Programme (UNEP), 2002; Montzka *et al.*, 2003]. Mixing ratios of CH₃Br, the most abundant bromine-containing gas in the free troposphere, increased steadily throughout most of the second half of the 20th century [Miller, 1998; Butler *et al.*, 1999; Sturges *et al.*, 2001]. Decreases have been noted for CH₃Br recently at two northern hemispheric (NH) locations

[Yokouchi *et al.*, 2002], although these results only loosely constrain global tropospheric trends of this short-lived, brominated gas.

2. Methods

2.1. Sampling and Analysis

[4] We measured brominated trace gases at ten remote sites across the globe: South Pole (90°S, 2837 m); Palmer Station, Antarctica (65°S, 64°W, 10 m); Cape Grim, Australia (41°S, 145°E, 94 m); American Samoa (14°S, 171°W, 77 m); Mauna Loa, USA (20°N, 156°W, 3397 m); Cape Kumukahi, USA (20°N, 155°W, 3 m); Wisconsin, USA (46°N, 90°W, 868 m); Harvard Forest, USA (43°N, 72°W, 340 m); Barrow, USA (71°N, 157°W, 8 m); and Alert, Canada (82°N, 62°W, 210 m). Whole air samples were pressurized into paired steel or glass flask an average of 2–4 times per month. All flasks were shipped to Boulder and analyzed for CH₃Br and halons by gas chromatography with mass spectrometry (GC-MS) and for halon-1301 by GC with electron capture detection [Montzka *et al.*, 1996; Butler *et al.*, 1998]. Results were retained when mixing ratios measured in simultaneously filled flasks were not measurably different, *i.e.*, <0.4 ppt for CH₃Br, <0.1 ppt for halon-1211, and <0.2 ppt for halon-1301 (95% of flasks for CH₃Br and halon-1301; 98% of all flasks for halon-1211). Approximately 1% of the remaining results were eliminated as outliers from all sites. CH₃Br results from South Pole are only from glass flasks; this gas is known to degrade over time in extremely dry steel flasks. Hemispheric means were estimated from three tropospheric boxes in each hemisphere based on measurements at sites located within them.

2.2. Standardization and Scale Consistency

[5] These results are referenced to standards prepared at ppt to ppm ($\mu\text{mol mol}^{-1}$) mixing ratios using gravimetric and static dilution techniques. The NOAA-CMDL scale for CH₃Br stems from ppm-level standards made in 1995 (1.2 ppm), 2001 (0.506 ppm and 0.565 ppm), and 2002 (0.862 ppm); analyses of these four standards by GC-MS throughout this period suggest consistency within $\pm 1\%$ and no systematic drift. Although large changes in CH₃Br mixing ratios have been observed in some Aculife-treated cylinders (Scott Specialty Gas Co., USA) our results through 1999 were based on a set of secondary standards that drifted only slowly over time (on the order of $1\text{--}2\%$ yr⁻¹). This drift was quantified and corrections were applied to the measured trends based upon multiple sets of primary and secondary standards made during 2000–2002 in Aculife-treated cylinders (dry air) and in electropolished, stainless steel containers (Essex Cryogenics, USA; humidified with 400–600 ppm H₂O). Similar drift corrections were derived from repeated analyses over periods of one to eight years of six archived, whole-air samples stored in electropolished, stainless steel

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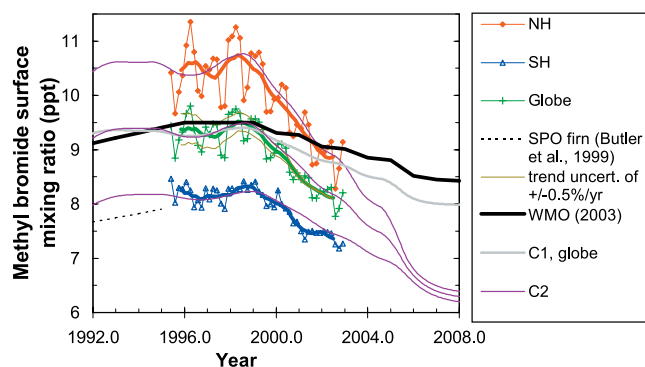


Figure 1. Measured bimonthly hemispheric and global mixing ratios of methyl bromide at Earth's surface (colored points connected by thin lines; colored thick lines are 12-month running means) are compared to a WMO global mean scenario [Montzka *et al.*, 2003] and box-model calculations (C_1 -mean global result shown only—And C_2 ; see text).

containers (Essex Cryogenics, USA, and SIS, USA). Consideration of these standards and archive samples suggests that our reference scale for CH_3Br was consistent within $0.5\% \text{ yr}^{-1}$ over the period 1995–2002.

2.3. Demonstrative Model Calculations

[6] Atmosphere and coupled ocean-atmosphere box-model calculations [Butler, 1994] were performed for CH_3Br with time-varying industrial emissions that were derived from production data reported to UNEP [1998], and additional constant emissions required to match the measured mixing ratios in 1995–1997. The calculation C_1 included a global lifetime of 0.7 yr, total CH_3Br emissions of 205 Gg yr^{-1} in 1992, and an emission fraction (f) of 0.5 [Williams *et al.*, 1999] for industrially produced CH_3Br applied to soils. Results from a range of calculations (represented by C_2) were derived with an [anthropogenic]/[global] emission fraction of 40–45% in 1996 (obtained with lifetimes of $0.8 < \tau < 1.5 \text{ yr}$ and corresponding releases from soils of $1.0 > f > 0.7$).

3. Results and Discussion

3.1. Methyl Bromide

[7] Our atmospheric measurements show that global mean mixing ratios of CH_3Br at Earth's surface began a steady decline after 1998 (Figure 1). The global annual mean of $8.1 (\pm 0.1) \text{ ppt}$ estimated from measurements at ten sites during 2002 was about $1.2 (\pm 0.3) \text{ ppt}$ (or about 13%) lower than the mean during 1995–1997. The global mean rate of change from mid-1999 to mid-2002 was $-0.35 (\pm 0.05) \text{ ppt yr}^{-1}$, which is a sharp contrast to the continuous increases reported for atmospheric CH_3Br throughout most of the 20th century [Khalil *et al.*, 1993; Miller, 1998; Butler *et al.*, 1999; Sturges *et al.*, 2001]. The observed decrease is substantially faster and larger than expected when compared to a WMO halocarbon scenario [Montzka *et al.*, 2003] that was used to project future stratospheric ozone abundances [WMO, 2003].

[8] Methyl bromide mixing ratios have not declined similarly at all sites across the globe; overall declines at NH surface sites ranged from 1.5 to 1.9 ppt during 1995–2002, or about two times larger than the concurrent changes observed

in the Southern Hemisphere. As a result, the hemispheric ratio (North/South) as estimated from NOAA-CMDL surface sites decreased from a value of 1.30 ± 0.03 during 1995–1997 to 1.23 ± 0.03 in 2002. The declines we have observed at arctic and midlatitude sites since 1999 are similar to those observed by Yokouchi *et al.* [2002] at Alert, Canada (82°N) and above Sagami Bay (35°N , from aircraft at 4000–7000 m).

[9] Global industrial production of CH_3Br has declined in recent years in response to restrictions outlined in the amended Montreal Protocol [UNEP, 2002]; global production of CH_3Br for all dispersive uses in 2000 was 18% lower than reported for the base year 1991, and preliminary data suggest production in 2001 that was 38% lower than in 1991 [UNEP, 1998; UNEP, 2002].

[10] Industrial production declines do not equate directly to atmospheric decreases for CH_3Br , however, because only a portion applied to soils is emitted to the atmosphere and because substantial amounts of this gas also are emitted from non-industrial activities [Mano and Andreae, 1994; Varner *et al.*, 1999; King *et al.*, 2000; Rhew *et al.*, 2001]. Current estimates suggest that emissions from industrial production were about $41 (30\text{--}62) \text{ Gg yr}^{-1}$ in 1992, or approximately 20 (10–40)% of the total emissions of 204 (157–327) Gg yr^{-1} implied by a total global lifetime of 0.7 (0.5–0.9) yr [Montzka *et al.*, 2003]. A similar percentage (15–40%) can be derived from measurements of CH_3Br in firn air [Montzka *et al.*, 2003].

[11] Differences between WMO, “best estimate” scenarios and the global measured trends reported here for CH_3Br suggest that the recent observed declines are not consistent with our current understanding of the global budget of this gas (Figure 1). Yokouchi *et al.* [2002] drew a similar conclusion from their measurements at two NH sites and box-model calculations. The measured hemispheric and global declines are more accurately simulated when fumigation-related emissions are assumed to have accounted for a larger fraction of total global emissions (40–45%) in the years before industrial production was reduced (Figure 1; calculations represented by C_2). These results suggest that the lifetime of CH_3Br is longer than 0.7 yr [also noted by Yokouchi *et al.*, 2002], and imply a mean fractional release after application to soils (f) larger than the 0.5 used in

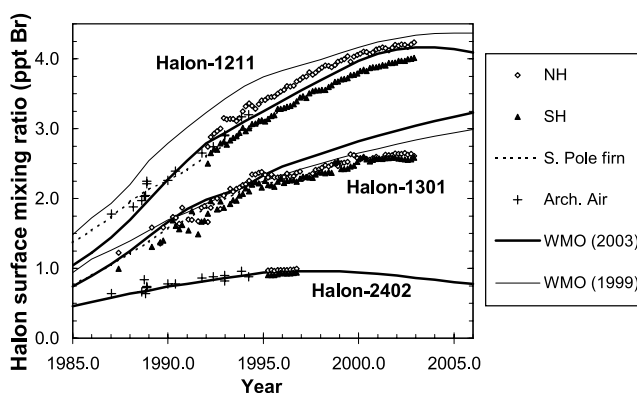


Figure 2. Measured hemispheric mixing ratios of the most abundant halons at Earth's surface (as ppt Br; points are bimonthly means unless from archive samples) compared to results from WMO scenarios [thin lines, Madronich *et al.*, 1999; thick lines, Montzka *et al.*, 2003].

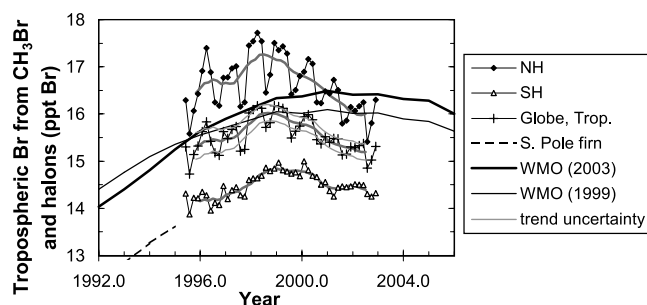


Figure 3. Mean tropospheric organic Br from NOAA-CMDL flask measurements of CH_3Br and the most abundant halons, and in recent WMO scenario calculations. To better approximate tropospheric means from surface measurements, tropospheric vertical gradients of 0–15% for CH_3Br [Schauffler *et al.*, 1999] were accounted for by multiplying measured surface mixing ratios by 0.93; no correction was applied to halon measurements. In this figure mixing ratios of halon-2402 were assumed constant after 1997 [Fraser *et al.*, 1999]. Trend uncertainty only shown on smoothed global results.

recent WMO reports. Data presented in UNEP [1998] suggest a mean value for f of about 0.7.

[12] While systematic trends in non-industrial emissions or sinks also could have affected the observed atmospheric decline of CH_3Br , no direct estimates of such changes are presently available. The timing of the decline in the two hemispheres and the substantially larger changes observed in the NH are both captured reasonably well with the C_2 model calculations, suggesting that the decline may result predominantly from reduced industrial emissions. Furthermore, we have not observed a similar decline from 1995–1997 to 2002 in mixing ratios of CH_3Cl , a gas that has many non-anthropogenic sources in common with CH_3Br .

[13] Barring substantial trends in natural fluxes, these results suggest that the sensitivity of atmospheric CH_3Br to changes in industrial production is higher than implied by current budget analyses. Our simple box-model calculations would suggest a global atmospheric lifetime ≥ 0.8 yr (for $f < 1.0$), a value for f larger than 0.5, and a substantially revised global budget. Given that these simple calculations contain much uncertainty, better quantification of such implications awaits more detailed modeling studies.

3.2. Halons

[14] Available measurement data indicate that halon-1211 (CBrClF_2) and halon-1301 (CBrF_3) accounted for much of the increase in atmospheric Br during the second half of the 20th century [Butler *et al.*, 1998; 1999; Fraser *et al.*, 1999; Sturges *et al.*, 2001]. Global mean mixing ratios of these gases continued to increase slowly in 2002 (Figure 2) owing to continued use of large halon stocks, continued production in developing countries, and halon atmospheric lifetimes that are relatively long [Butler *et al.*, 1998; Fraser *et al.*, 1999; Montzka *et al.*, 2003]. From mid-1999 to mid-2002, atmospheric Br from the sum of these halons increased at a mean rate of $0.1 \text{ ppt Br yr}^{-1}$, most of this growth coming from increases in halon-1211. This rate is slower than was observed in the mid-1990s when Br from these gases was increasing at rates between 0.2 and 0.3 ppt yr^{-1} .

[15] Halon scenarios from past WMO Ozone Assessments are roughly consistent with currently observed mixing ratios and trends (Figure 2), although large uncertainties regarding the size of unemitted stocks and the lifetime of halon-1211 make accurate projections difficult [Madronich *et al.*, 1999; Montzka *et al.*, 2003]. Despite this, the projections, and the fact that halon production in both developed and developing countries is now limited [UNEP, 2002], suggest that accumulation rates for these halons will continue to decrease in the coming years.

[16] Industrial production of other halons such as halon-2402 ($\text{C}_2\text{Br}_2\text{F}_4$) and halon-1202 (CBr_2F_2) has contributed some additional Br to the global atmosphere [Butler *et al.*, 1998; Fraser *et al.*, 1999], but these additional gases have not substantially affected recent trends in atmospheric Br.

3.3. Other Brominated Gases

[17] Short-lived gases with mostly natural sources, such as CHBr_3 and CH_2Br_2 , can be transported rapidly to the stratosphere and contribute to ozone-depleting Br [Schauffler *et al.*, 1999; Pfeilsticker *et al.*, 2000]. Some Br (0–6 ppt) may also reach the stratosphere as inorganic Br from the photochemical oxidation of short-lived gases as they are transported through the troposphere [Pfeilsticker *et al.*, 2000; Ko *et al.*, 2003]. Although atmospheric Br from these gases may be variable on interannual time scales, Antarctic firm air data suggest minimal long-term changes throughout the second half of the 20th century [Sturges *et al.*, 2001]. Any systematic trends in emissions of these gases would have to have been inordinately large to offset the decline noted here for tropospheric Br from halons and CH_3Br .

3.4. Tropospheric Organic Bromine

[18] The sum of Br from the most abundant halons and CH_3Br reached a peak in 1998 and declined thereafter in the troposphere at a mean rate of $-0.25 \pm 0.09 \text{ ppt yr}^{-1}$ (Figure 3; mean over 1999–2002). This decline is driven entirely by

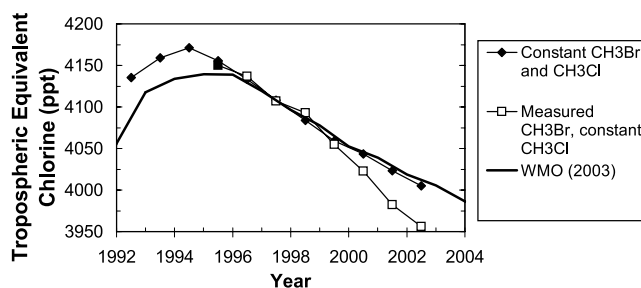


Figure 4. Changes in the global tropospheric burden of both brominated and chlorinated ozone-depleting gases in recent years expressed as equivalent chlorine (where $\text{ECl} = \text{Cl} + 45 \times \text{Br}$). Data for Cl included in this calculation are updates to measurements described previously [Montzka *et al.*, 1996; 1999] of CFC-11, -12, and -113; methyl chloroform; carbon tetrachloride; and HCFC-22, -141b, and -142b. ECl is calculated considering measured tropospheric mixing ratios of these gases plus those of halon-1211 and halon-1301, and either (1) constant mixing ratios for CH_3Br and CH_3Cl (mixing ratios were scaled by the measured global mean for these gases over 1995–1997), or (2) constant CH_3Cl and measured changes in CH_3Br , and (3) WMO scenario Ab [Montzka *et al.*, 2003].

the decreases observed for CH_3Br . The result suggests that the total amount of Br entering the stratosphere reached a plateau in 1998 and has since decreased. Tropospheric Br from CH_3Br , halon-1211, and halon-1301 during 2002 was about 5% (or 0.8 ± 0.2 ppt) below the amounts measured in 1998–1999.

[19] The declines in Br since 1998 are substantial compared to the changes in Cl over this period. Tropospheric Cl from long-lived gases was decreasing at 22 ppt yr^{-1} in 2000, and this rate has become smaller since then as the influence of methyl chloroform has diminished [Montzka et al., 2003]. Considering that Br is about 45 times more efficient at depleting stratospheric ozone than Cl on average [Daniel et al., 1999], the observed rate of change in tropospheric organic Br since 1998 corresponds to a decline of about 11 ppt yr^{-1} in Cl equivalents, or about half as large as the mean decline observed for Cl contained in long-lived chlorinated gases during this period. An updated calculation of tropospheric equivalent chlorine ($\text{ECI} = \text{Cl} + \text{Br} \times 45$) that includes our global measurements of CH_3Br shows an overall decline by 2002 that is 25–30% larger than a recent WMO Ozone Assessment scenario or analyses in which constant CH_3Br mixing ratios are assumed (Figure 4). Changes we have measured for mixing ratios of CH_3Cl during 1995–2002 (not shown) have not affected the systematic decline in ECI, but they have added to its interannual variability.

[20] Sustained declines for atmospheric Br in the near future depend upon changes in CH_3Br continuing to offset the small increases observed for halons. The recent measured rates of change for halons are similar to or less than those projected in recent WMO Ozone Assessment scenarios (Figure 2), and they are expected to diminish further as stocks are depleted. Furthermore, global production of halons and CH_3Br is unlikely to increase in coming years because limits to production outlined in the Montreal Protocol now apply to both developed and developing nations (as of January 2002) [UNEP, 2002]. Even with growth rates for CH_3Br and halons that are enhanced relative to those we report here, Br in WMO scenarios does not increase after 2002 (Figure 3). Accordingly, the fairly rapid decline in atmospheric CH_3Br has led to a decrease in atmospheric Br sooner than expected. In the absence of large changes in natural fluxes, continued adherence to restrictions in the Montreal Protocol should result in sustained declines for Br in the future to levels lower than projected previously.

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References

- Butler, J. H., The potential role of the ocean in regulating atmospheric CH_3Br , *Geophys. Res. Lett.*, **21**, 185–188, 1994.
Butler, J. H., S. A. Montzka, A. D. Clarke, J. M. Lobert, and J. W. Elkins, Growth and distribution of halons in the atmosphere, *J. Geophys. Res.*, **103**, 1503–1511, 1998.

- Butler, J. H., et al., A twentieth century record of atmospheric halocarbons in polar firm air, *Nature*, **399**, 749–755, 1999.
Cunnold, D. M., et al., GAGE/AGAGE measurements indicating reductions in global emissions of CCl_3F and CCl_2F_2 in 1992–1994, *J. Geophys. Res.*, **102**, 1259–1269, 1997.
Daniel, J. S., S. Solomon, R. W. Portmann, and R. R. Garcia, Stratospheric ozone destruction: The importance of bromine relative to chlorine, *J. Geophys. Res.*, **104**, 23,871–23,880, 1999.
Fraser, P. J., D. E. Oram, C. E. Reeves, S. A. Penkett, and A. McCulloch, Southern Hemispheric halon trends (1978–1998) and global halon emissions, *J. Geophys. Res.*, **104**, 15,985–15,999, 1999.
Khalil, M. A. K., R. A. Rasmussen, and R. Gunawardena, Atmospheric methyl bromide: Trends and global mass balance, *J. Geophys. Res.*, **98**, 2887–2896, 1993.
King, D. B., J. H. Butler, S. A. Montzka, S. A. Yvon-Lewis, and J. W. Elkins, Implications of methyl bromide supersaturations in the temperate North Atlantic Ocean, *J. Geophys. Res.*, **105**, 19,763–19,769, 2000.
Ko, M. K. W., et al., Very short-lived halogen and sulfur substances, Chapter 2, in *Scientific Assessment of Ozone Depletion: 2002, Rep. Global Ozone Res. and Monitor. Proj.*, Vol. No. 47, World Meteorol. Organ., Geneva, Switzerland, 2003.
Madronich, S., et al., Halocarbon scenarios for the future ozone layer and related consequences, Chapter 11, in *Scientific Assessment of Ozone Depletion: 1998, Rep. Global Ozone Res. and Monitor. Proj.*, Vol. No. 44, World Meteorol. Organ., Geneva, Switzerland, 1999.
Mano, S., and M. O. Andreae, Emission of methyl bromide from biomass burning, *Science*, **263**, 1255–1258, 1994.
Miller, B. R., Abundances and Trends of Atmospheric Chlorodifluoromethane and Bromomethane, Ph.D. thesis, Univ. of California, San Diego, 1998.
Montzka, S. A., et al., Decline in the tropospheric abundance of halogen from halocarbons: Implications for stratospheric ozone depletion, *Science*, **272**, 1318–1322, 1996.
Montzka, S. A., et al., Present and future trends in the atmospheric burden of ozone-depleting halogens, *Nature*, **398**, 690–694, 1999.
Montzka, S. A., et al., Controlled substances and other source gases, Chapter 1, in *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Res. and Monitor. Proj.*, Vol. No. 47, World Meteorol. Organ., Geneva, Switzerland, 2003.
Pfeilsticker, K., et al., Lower Stratospheric organic and inorganic bromine budget for the arctic winter 1998/99, *Geophys. Res. Lett.*, **27**, 3305–3308, 2000.
Rhew, R. C., B. R. Miller, M. K. Vollmer, and R. F. Weiss, Shrubland fluxes of methyl bromide and methyl chloride, *J. Geophys. Res.*, **106**, 20,875–20,882, 2001.
Schauffler, S. M., et al., Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, **104**, 21,513–21,535, 1999.
Sturges, W. T., et al., Methyl bromide, other brominated methanes, and methyl iodide in polar firm air, *J. Geophys. Res.*, **106**, 1595–1606, 2001.
United Nations Environment Programme, 1998 Assessment of alternatives to methyl bromide, Methyl Bromide Tech. Options Comm., Nairobi, Kenya, 1998.
United Nations Environment Programme, Fourteenth meeting of the parties to the Montreal Protocol on substances that deplete the ozone layer, *Rep. U.N. Environ. Program. Ozone Secr. Pro14/3*, 18 October, 2002.
Varner, R. K., P. M. Crill, and R. W. Talbot, Wetlands: A potentially significant source of atmospheric methyl bromide and methyl chloride, *Geophys. Res. Lett.*, **26**, 2433–2435, 1999.
Williams, J., N.-Y. Wang, and R. J. Cicerone, Methyl bromide emissions from agricultural field fumigations in California, *J. Geophys. Res.*, **104**, 30,087–30,096, 1999.
World Meteorological Organization, Scientific Assessment of Ozone Depletion: 2003, *Rep. Global Ozone Res. and Monitor. Proj.*, Vol. No. 47, 498 pp., World Meteorol. Organ., Geneva, Switzerland, 2003.
Yokouchi, Y., D. Toom-Saunty, K. Yazawa, T. Inagaki, and T. Tamaru, Recent decline of methyl bromide in the troposphere, *Atmos. Environ.*, **36**, 4985–4989, 2002.

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